Raman Chemical ID in the Presence of Fluorescence

Introduction

Ahura Corporation's *First* **Defender**[TM] handheld Raman material identification system was a ground-breaking addition to the First Responder toolbox. The ability to rapidly perform material identification with a 4lb battery operated device in a non-contact fashion was a significant advantage over existing IR spectroscopy tools. This application note discusses the phenomenon of fluorescence, and the impact it has on FirstDefender results.

Raman and Fluorescence

Figure 1 illustrates the difference between Raman and fluorescence emission. In short, fluorescence is characteristic of the electrons populating a molecule, while Raman is characteristic of the individual inter-atomic bonds. Since the electrons carry little information about the identity of the molecule, the fluorescence signal tends to be broad and nondescript, in contrast to the Raman signal which has many sharp characteristic bands relating to specific molecular structure.

The fluorescence phenomenon varies widely in intensity from molecule to molecule. Some strongly fluoresce, while many others show no evidence of the effect. Fluorescent molecules and materials affect the performance of the *First* **Defender** (and any other Raman instrument) in two primary ways.
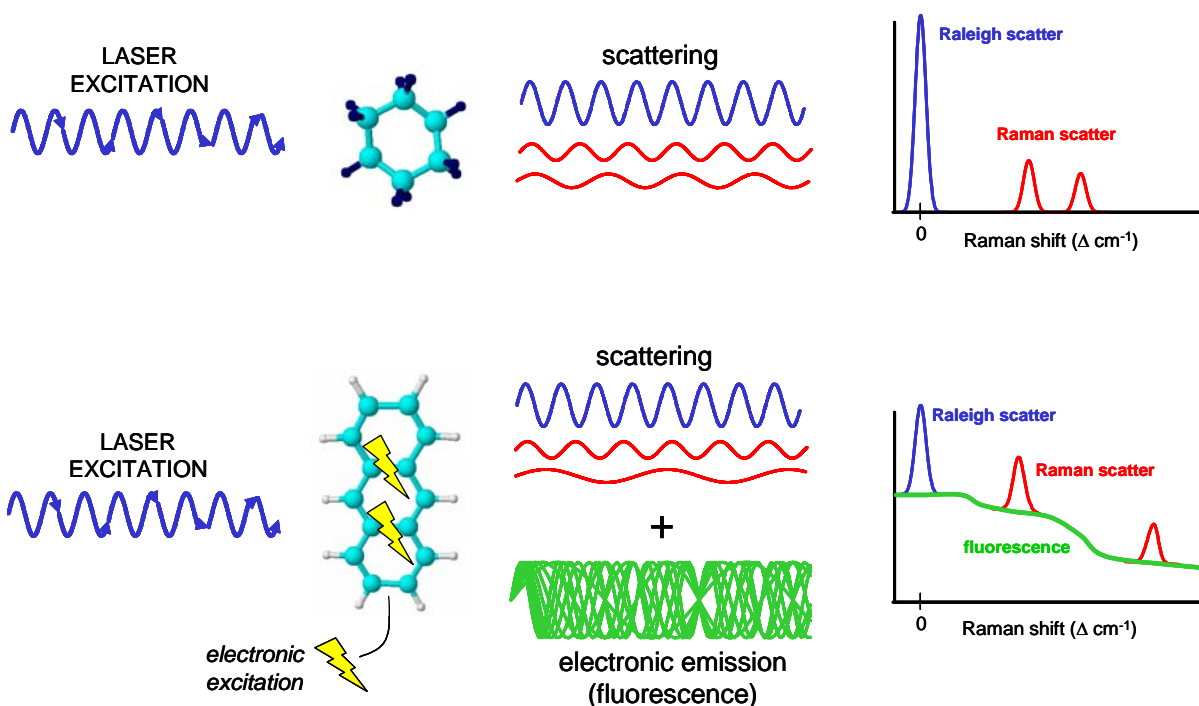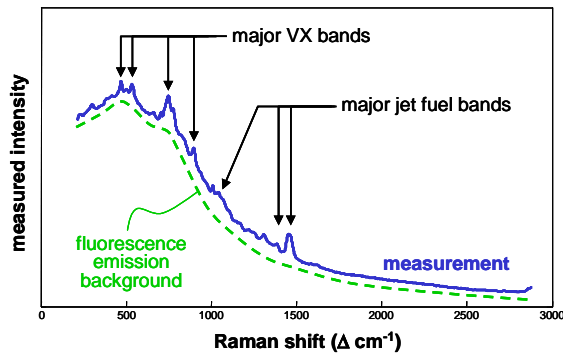

Figure 1. Illustration of the phenomena, and spectral result of Raman scattering and fluorescence emission.

Figure 2. Measurement (blue) of a fluorescent mixture of VX nerve agent in JP8 jet fuel. VX is approximately 25% by volume. The strong fluorescence background is highlighted by the dashed green line.

The first effect of this fluorescence is that the Raman signature of the material(s) will 'ride' on top of the broad nonspecific baseline of fluorescence. This is a fatal condition for most traditional Raman and FTIR spectrum searching software because it makes no distinction between fluorescence signal, and Raman signal. These software packages tend to produce very low 'HQI' (hit quality index) values even under mildly fluorescent conditions, making reliable material identification all but impossible for the user. In contrast, Ahura's proprietary DecisionEngine™ software is not fooled by fluorescence. Instead, the software automatically corrects for fluorescence and similar annoyances, enabling reliable material identification in most cases with no user intervention. An example of the DecisionEngine's ability to work with fluorescent materials is shown in **Figure 2**. The spectrum shown was acquired at the Army's, Edgewood Chemical and Biological Center (ECBC), and the sample was a mixture of VX, a highly toxic nerve agent, diluted with jet fuel such that VX was approximately 25% by volume. Jet fuel and some VX by-products are known to be highly fluorescent, and the tell-tale broad background of fluorescence is very apparent in **Figure 2**. Although these conditions would preclude identification of VX by Raman systems that use conventional library search routines, Ahura's DecisionEngine MX had no difficulty determining that the unknown was actually a mixture of VX and jet fuel. With other portable Raman systems less adept at handling fluorescence, the VX would have been difficult to detect. The lack of mixture analysis software is a critical limitation of other currently available FTIR and Raman systems. This capability is covered in a more detail in *"On-Scene Mixture Analysis with DecisionEngineTM MX"*

The second effect of fluorescence is that it can lead to a noisier Raman signature. This is a bit like listening to a radio station that has excess static. Although the static is unpleasant to listen to, the human brain usually has little difficulty recognizing what is being said – one just has to listen a little bit more carefully. Ahura's DecisionEngine software does exactly that. Users will sometimes notice that for particularly highly fluorescent materials, FirstDefender will take longer to reach a conclusion than for non-fluorescent materials. In some particularly noisy cases, the system will eventually 'stop listening' and report "no match found," rather than inconvenience the user with an excessively long measurement.

Summary

While fluorescence is a complicating factor in material identification with Raman spectroscopy, it is by no means a barrier. With intelligent embedded software, and carefully designed spectroscopic analysis algorithms, reliable results can often still be obtained from most fluorescent media.